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HYDROGEN PEROXIDE TANK SAFETY

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Naval Research Laboratory

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exposure but that one-inch insulation would protect the tank and contents for at least 30 minutes. Additional calculations, combined with experimental H_2O_2 decomposition rates, predict that the critical self-heat temperature for one-inch insulation, while lower than that for the bare tank, would be acceptable.

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HYDROGEN PEROXIDE TANK SAFETY

Robert N. Hazlett, Jack P. Stone and James M. Hall

INTRODUCTION

Hazardous chemicals are an important article of commerce and large quantities are being shipped by water and overland. Recent accidents with some of these materials (1,2) stimulated further examination of the hazards associated with the transport of oxidizers, corrosive chemicals and pressurized and liquified gases. The United States Coast Guard has the responsibility for regulating water transport of such chemicals in U. S. ports and inland waters. In the present instance, they are concerned with the hazards associated with proposed containers (See Appendix I) for transporting 4,000 gallons of 70 percent hydrogen peroxide, particularly the behavior of such a container and its contents in a severe fire when on the deck of a ship. This report describes work supported by the U.S. Coast Guard Office of Research and Development at NRL to address this hazard.

The proposed H_2O_2 tanks in which the foreign product will be shipped will be constructed from 99.5% aluminum. The Coast Guard does not normally allow the use of aluminum for tank construction because of its poor high temperature strength. In this case, however, aluminum is necessary to minimize the decomposition rate of the cargo. The calculations in this work are engineering estimates made to study the effect of a vigorous fire on a nominal 4,000 gallon bare aluminum container of 70% hydrogen peroxide. In addition, the effect of two different insulation thicknesses on heat transfer from a fire to the tank was estimated. We also experimentally determined the rate of decomposition of a stabilized 70%

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hydrogen peroxide over the temperature range 122-275°F (50-135°C), the latter temperature being 18°F (10°C) above the normal boiling point. The experimental decomposition rate was utilized to calculate gas venting requirements for the 4,000 gallon tank and the heat liberated by H₂O₂ decomposition at different temperatures. The latter results were used along with heat transfer rates from bare and insulated tanks in a post-fire regime to estimate self-heat temperatures for the H₂O₂ container.

DECOMPOSITION RATES

The readiness with which hydrogen peroxide may be decomposed into water and molecular oxygen is a characteristic which has been familiar since the discovery of this substance. It is a property both useful and troublesome and one brought about in many ways. Rates of decomposition vary over an extremely broad range from the exceedingly low values obtainable with carefully purified material under optimum conditions to the very rapid decomposition required in the use of concentrated peroxide as a rocket propellant. Controlling factors include temperature, pH, catalysis and radiation. Typical catalysts are heavy and transition metals such as silver, copper, iron, chromium and mercury (3). Catalysts may be either homogeneous or heterogeneous.

The importance of concentration of hydrogen peroxide solutions in relation to the hazards of decomposition is shown by the fact that above 65 weight percent the heat liberated is sufficient to vaporize all the water present plus that formed by decomposition (4). The adiabatic decomposition temperature of 90 percent peroxide is 1380°F (750°C). Normally in storage the heat liberated is dissipated to the surroundings with a temperature rise of 1°C or less.

All hydrogen peroxide solutions decompose during storage. Decomposition is minimized (5) by: (a) the initial production of hydrogen peroxide in a state of high purity, (b) the addition of certain substances, called stabilizers, which counteract the effect of catalytic impurities or container surfaces, and (c) control of the environment to which the hydrogen peroxide is exposed. Cleanliness in all handling procedures is essential.

Stabilizers include sodium stannate, sodium pyrophosphate and 8-hydroxyquinoline (6,7). The nature of container surfaces is critical to peroxide stability. Suitable materials include pure aluminum, pure tin and Pyrex glass. In addition to container wall characteristics, surface/volume ratio is significant.

Pure hydrogen peroxide, in the absence of catalytic contaminants and in a thoroughly clean container of noncatalytic material, is a surprisingly stable substance. Typical data with high quality unstabilized hydrogen peroxide indicate a decomposition rate not in excess of 0.002% per hour for 90% peroxide at 50°C (8). In the presence of a small quantity of stabilizer this value may be reduced to 0.0003% per hour at 50°C (3,8).

Temperature has an exponential effect on the decomposition rate of pure, unstabilized hydrogen peroxide. The effect is defined by the expression (3,9)

$$(T_2 - T_1) \log a = 10 \log(k_2/k_1),$$

where T_2 and T_1 are temperatures in °C, and k_2 is the decomposition rate at T_2 and k_1 is the rate at T_1 . The temperature coefficient "a" has been found to have a value of 2.2 ± 0.1 over the range 50° to 90°C (8). This indicates that the rate more than doubles for each 10°C rise in temperature, or increases about fifty-fold for the interval 50° to 100°C. Some typical decomposition data for 90% hydrogen peroxide are given in Table 1 (7,8).

The intent of the present work was to investigate decomposition rates of 70% hydrogen peroxide over a temperature range up to and above the normal boiling point (125°C for 70 wt-%). Previously reported work on hydrogen peroxide stability was done largely with 90% material. Reproducibility of results was a problem at 100°C and above and a lower temperature was commonly employed, for example 50°C. In the present problem decomposition rates of particular significance are those at: (a) the ambient temperatures encountered in transportation and (b) the temperatures resulting from a fire situation, especially the decomposition rate up to the

TABLE 1

Stability of 90% Hydrogen Peroxide At Various Temperatures

<u>Temperature</u>	<u>Approx. Rate of Decomposition</u>
30°C (86°F)	1% per year
66°C (151°F)	1% per week
100°C (212°F)	2% in 24 hours
140°C (284°F)	Decomposes rapidly with boiling

TABLE 2

Summary of Tests on Decomposition Rate
of 70% Hydrogen Peroxide

<u>Temp., °C</u>	<u>Decomposition Rate, %/day</u>	
	<u>By O₂ Evolution</u>	<u>By Wt. Loss</u>
50	0.0144	0.012
	0.0148	0.020
75	0.0744	0.079
	0.0747	0.082
95	0.454	0.413
	0.400	0.400
110	0.99	---
	1.02	1.00
125	3.75	2.90
	3.96	3.93
135	8.13	---
	5.70	---

boiling point at the relief pressure of the 4,000 gallon container. Pressure is said to have no effect on the rate (7).

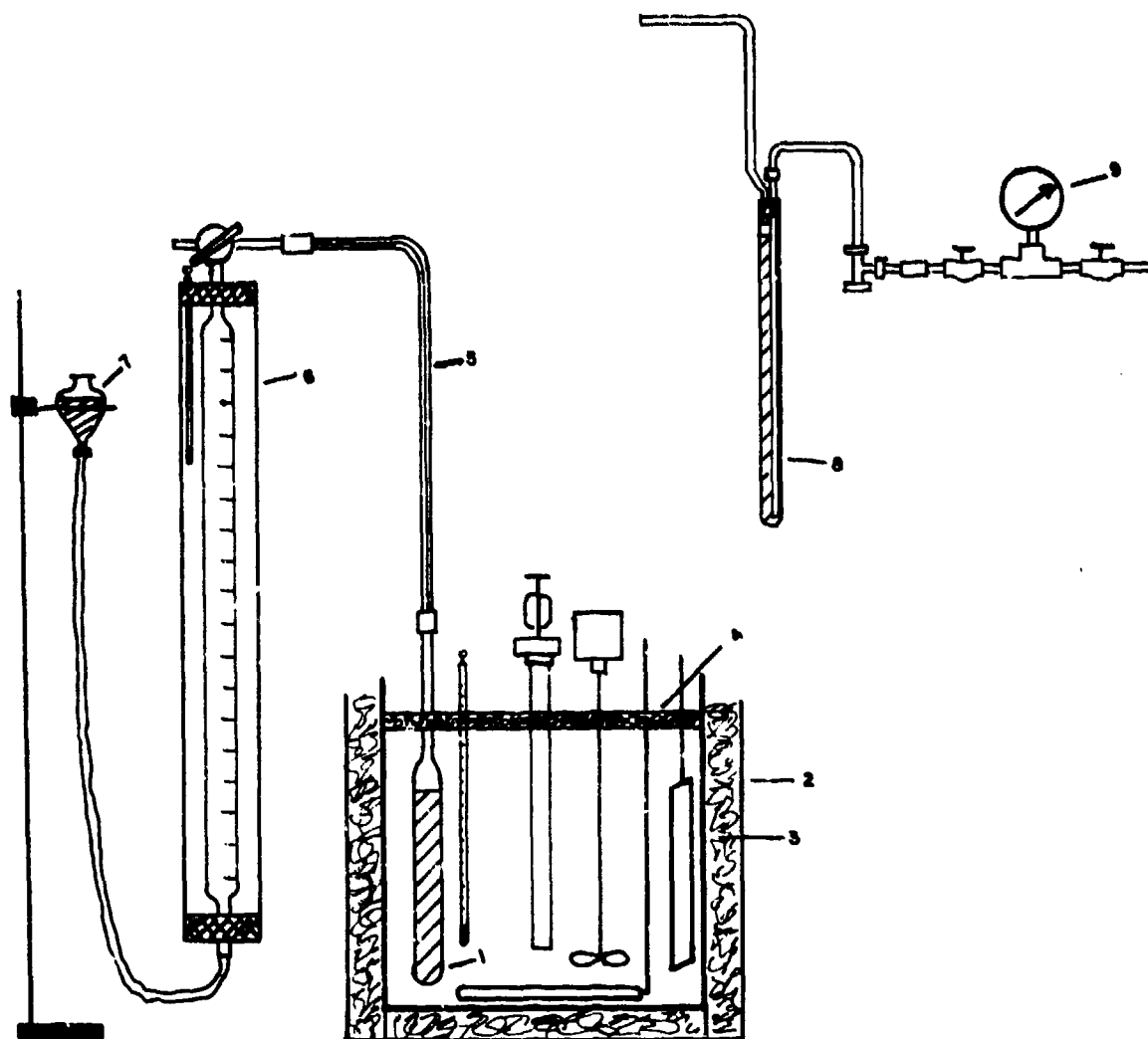
Experimental

Procedure - The product used in the decomposition tests was a 70% hydrogen peroxide obtained from a U. S. company. Analysis gave a concentration of 70.0 weight percent.

Three methods for the determination of decomposition rates were employed: measurement of the volume of oxygen evolved, of the weight loss, and of the change in peroxide concentration. The first proved the most satisfactory. The very small weight changes observed made the second method marginal. The third method was unsatisfactory due in part to the small concentration changes experienced. Furthermore, an analytical precision of not less than 0.01% was required and this was not obtainable, even with burdensome replicate analyses. Both the second and third methods are more appropriate for long-term tests or tests where large changes in concentration occur.

In this report decomposition rate is defined as a percent of the peroxide originally present decomposing in unit time. Thus, rate is a percent of a percentage. The percent decomposed per hour or day must be distinguished from the percent concentration change. For example, starting with 70.0% peroxide a rate of decomposition of 1%/day would indicate a concentration of 69.3% remaining after 24 hours.

In the oxygen evolution or gasometric method, a cleaned, noncatalytic vessel containing the peroxide sample is held at a constant temperature and the oxygen evolved is collected at constant pressure (1 atm.) in a gas buret over water. From the volume of oxygen, allowing for saturation with water vapor and correcting to standard conditions, the amount of peroxide decomposed can be calculated. Figure 1, shows the type of apparatus used for tests below 100°C. The reaction vessel, connected through capillary tubing to a water-jacketed gas buret



- | | |
|-----------------------------------|--------------------------------|
| 1. REACTION (DECOMPOSITION) TUBE) | 6. 100 ML GAS BURET WITH |
| 2. CONSTANT TEMPERATURE BATH | WATER JACKET |
| 3. INSULATION | 7. WATER LEVELING BULB |
| 4. SHREDDED POLYSTYRENE PLASTIC | 8. 25 CM MERCURY MANOSTAT (FOR |
| 5. PYREX CAPILLARY TUBING | TESTS ABOVE BOILING POINT) |
| | 9. PRESSURE GAGE |

Fig. 1 - Apparatus for decomposition rates by gas evolution

with leveling bulb, is supported in an insulated thermostated water bath. Our reaction vessels were heavy wall Pyrex tubes 9 inches long by 1 inch O.D. An integral upper tube 8 inches long by 1 cm O.D. extending above the bath, permitted any escaping water vapor to condense and flow back. Volume of these tubes was 57 ml. Temperature of the bath was controlled to approximately 0.2°C. In the tests at 75° and 95°C a layer of shredded polyfoam plastic effectively retarded evaporation from the bath. The reaction tubes were cleaned by standing filled with concentrated nitric acid for 24 hours or more followed by thorough rinsing with distilled water. They were then pre-conditioned by standing with 70% hydrogen peroxide. For the tests above 100°C, the reaction tube was supported in a well in an insulated aluminum block furnace. The well was filled with a silicone oil. Temperature was controlled to 0.5°C. Temperature of the silicone oil was measured with thermometers and recorded with a thermocouple. Tests at 135°C were conducted under a pressure of 5 psig since 135° is above the normal boiling point of 70% hydrogen peroxide. The pressure was established and controlled by a 25 cm mercury column interposed between the reaction tube and the capillary leading to the gas buret. A pressure gage was connected by means of a polyethylene tee to permit leak testing and to monitor the reaction pressure. In the 135°C tests, an air stream directed at the narrow upper part of the reaction tube cooled it to prevent loss of any water vapor. This precaution applied only to the weight loss method of measuring the decomposition.

Weight of the reaction tube was measured on an oversized analytical balance accurate to about 0.5 mg. Weight losses were usually under 100 mg and rates calculated therefrom had an accuracy of 5 to 10%. Peroxide concentration was determined by titration of a small sample or aliquot with standard 0.1 N ceric ammonium sulfate. Precision of the analysis was 0.2% or better. However, this equated to a precision of only about ±50% in the calculated decomposition rate. Thus the titration method is unsuitable with small changes in concentration of peroxide.

The time period of measurement ranged from 2 weeks at 50°C to 4 hours at 135°C. In addition to the overall average rates reported in Table 2, the incremental rate was observed to ensure its constancy.

Results - A summary of experimental results is presented in Table 2 and Figure 2. It is apparent that duplicate tests agreed well, with one exception, and that the data from weight loss supported the more accurate results from oxygen evolution very well. The decomposition rate of 0.014%/day at 50°C in Table 2 agrees well with previously published data since it lies between minimum reported values for stabilized and unstabilized hydrogen peroxide (8). It is concluded that the peroxide we used must be stabilized. However, no chemical tests for the presence of stabilizers were made. Figure 2 is a plot of the decomposition rates calculated from oxygen evolution versus temperature. The slope of the graph equals the log of the temperature coefficient "a". We found a value of 2.08 for "a" in this work.

Conclusions - In translating the above results to the 4,000 gal aluminum peroxide tank, several points must be kept in view. First, the data above represent ideal or minimum values for the decomposition. Second, stability of the foreign peroxide is not known. Further, factors such as smoothness and catalytic nature of the container surface, pre-conditioning of the surface, the presence of any dirt or contaminant and the surface/volume ratio can have significant effects on decomposition rates (8,10).

HEAT TRANSFER ANALYSIS

Since hydrogen peroxide solutions decompose with evolution of heat at ordinary temperatures and at rates which increase with temperature, its storage tank must lose heat at some minimal rate. Otherwise, the tank self-heats. According to Shanley (4), the hazard created by self-heating is due to pressure rise in the tank, the final outcome of which depends primarily on the H_2O_2 concentration. For example, adiabatic decomposition of 90 wt % H_2O_2 can produce a temperature of 1380°F (750°C),

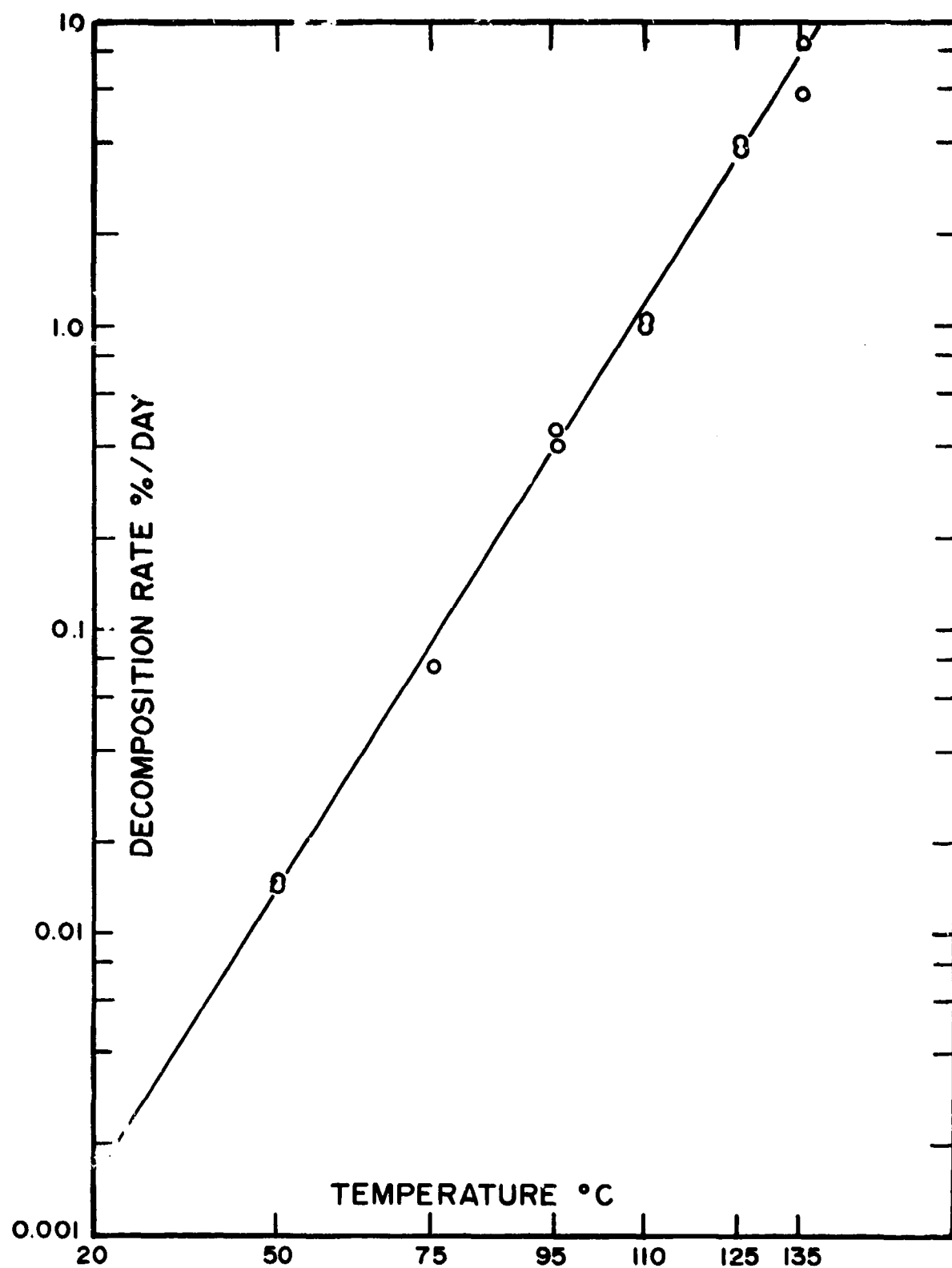


Fig. 2 - The decomposition rates of 70% hydrogen peroxide

while 12 wt % produces 212°F (100°C). It is important then that H₂O₂ tanks lose heat. In fact, Shanley recommends that storage tanks be bare.

On the other hand, if H₂O₂ tanks are involved in an intense, unwanted fire, uninsulated tanks are rapidly heated and, as this analysis indicates, may fail in less than 5 minutes.

In this study, we consider conditions of self-heating and of fire involvement for the 4,000 gallon, 99.5% aluminum tank containing 70 weight percent H₂O₂ aqueous solution, as described by the Eisenbahn-Verkehrsmittel Aktiengesellschaft (Eva) (11). Both uninsulated (bare) and insulated (2.76 inches thick and 1.0 inch thick) tank conditions are included. In fire involvement, we consider a suggested period of 30 minutes.

Self-Heating Conditions

For usual ambient H₂O₂ temperatures, a heat balance for the tank of H₂O₂ exists so that the heat lost from the tank equals the heat gained due to decomposition of the H₂O₂, and an equilibrium H₂O₂ temperature is established. However, if H₂O₂ decomposition were to release more heat than could be dissipated, the H₂O₂ temperature would rise and create a self-accelerating decomposition.

In Figure 3, heating and cooling curves are presented for the three tank conditions: bare, 2.76-inch (70 mm) insulation, and 1.0-inch (25 mm) insulation. A thermal conductivity of 0.043 BTU/(hr)x(ft)x(°F) was used for the insulation. Curves labeled A and B are heating curves that result from the H₂O₂ decomposition. Curve A shows the heat-release rate calculated for a decomposition rate of 0.9% per year at 77°F (25°C) (NRL measurement) as the ordinate versus the average temperature of the H₂O₂ solution as the abscissa. Curve B represents a decomposition rate arbitrarily chosen as five times the rate of curve A since impurities in the H₂O₂ solution usually increase the decomposition rate.

The cooling curves shown in Figure 3 are numbered.

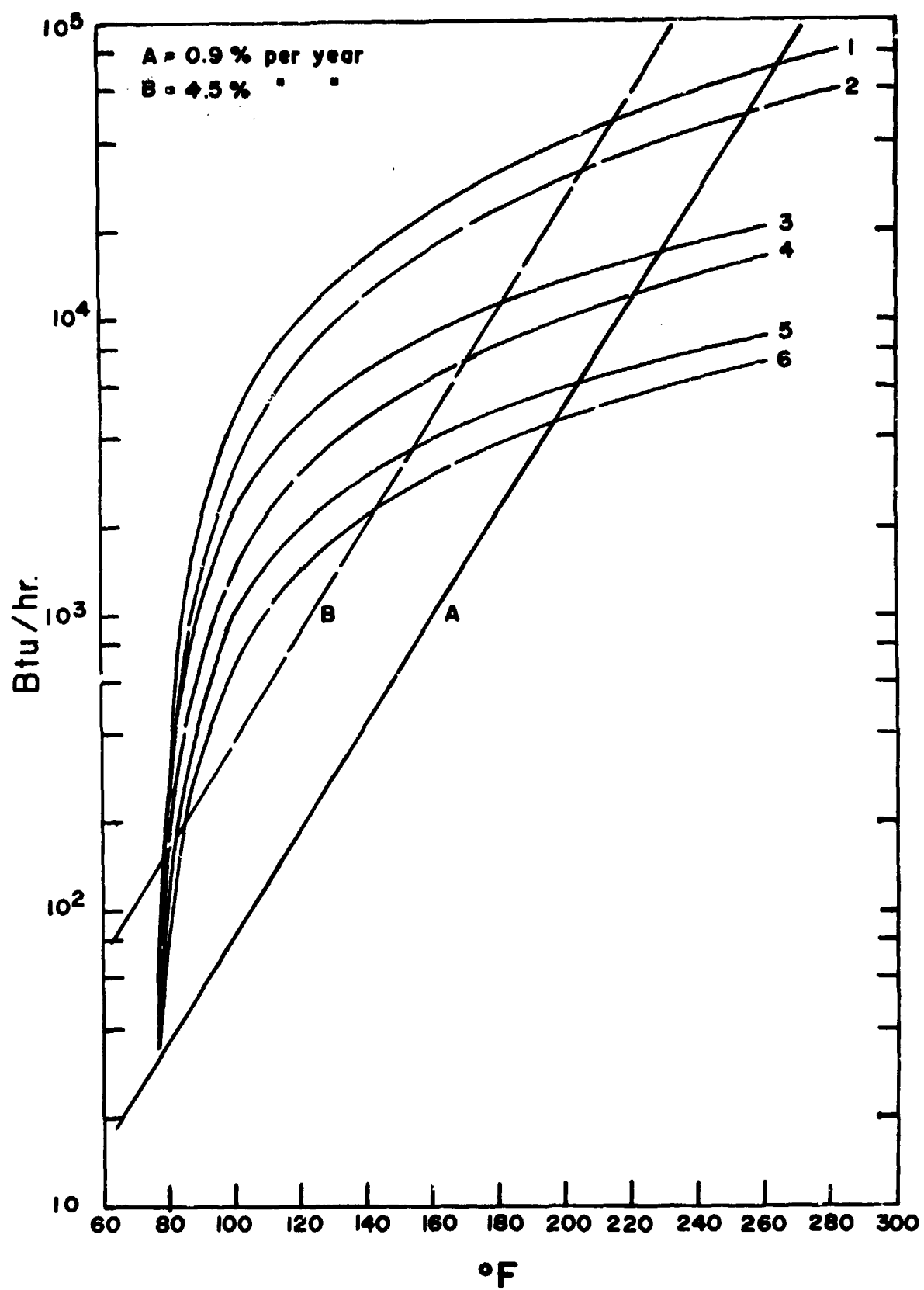


Fig. 3 - Heat balance

Curves 1 and 2 are estimates of heat lost from the bare tank. For these curves, the ordinate is the rate of heat lost from the tank, and the abscissa is the temperature of the H_2O_2 solution. For curve 1, we assume that the tank loses heat by radiation as well as by free convection, whereas for curve 2, heat is lost only by free convection. Curves 3 and 4 show similar assumptions for the heat losses with 1 inch of insulation and curves 5 and 6 with 2.76 inches of insulation. These cooling curves are calculated with the assumption that ambient temperature is 78°F (25.5°C).

Intersections of the heating and cooling curves in Figure 3 at the lower temperatures represent predicted equilibrium temperatures where heat released by decomposition equals heat lost by the tank, while the intersections at the higher temperatures are those predicted for the start of accelerated self-heating. So long as H_2O_2 remains below these limiting temperatures, the tank will cool back to equilibrium with its surroundings (78°F for these cooling curves). Appendix I shows dimensions of the tank and calculations for Figure 3 are given in Appendix II, Part I.

Fire Involvement

If a 4,000 gallon tank containing 70 wt-% H_2O_2 , as described, is involved in an intense, enveloping fire, what happens during the first 30 minutes? In answer to this question, we attempt to predict time and events as based on available information (12-16) and on calculation. Such hazardous events may occur as: (a) heat of H_2O_2 above the limiting temperature, (b) release of H_2O_2 into a fire by the tank-pressure-relief system, (c) tank rupture, and (d) explosion of H_2O_2 vapor.

Bare Tank - In Figure 4, a graphical summary of predictions is presented for fire involvement for the bare tank; temperature is plotted versus time. It is assumed that the fire begins at time zero ($\theta = 0$) and that heat flux in the fire remains constant in all directions $(q/A = 34,500 \frac{Btu}{(hr)(ft)^2})$. Further, it is

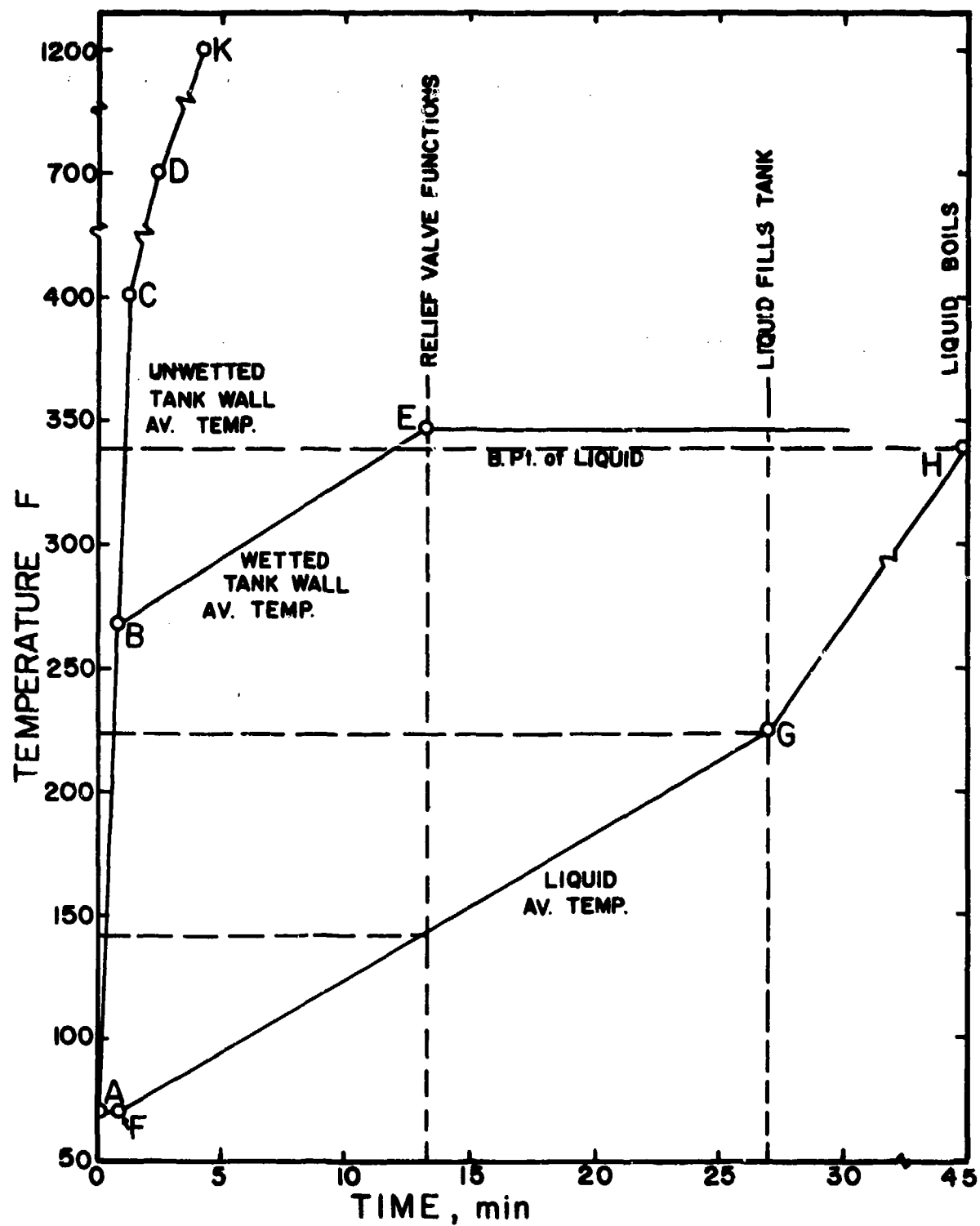


Fig. 4 - Heating of bare tank

assumed that the tank is filled at an ambient temperature of 68°F (20°C) and 1 atmosphere pressure with an ullage of 5%. Other pertinent assumptions and calculations are given in Appendix II, Part II.

At point A in Figure 4 an ambient temperature of 68°F (20.0°C) and zero time marks the start of the heating of the tank wall. For a period of about 0.72 minutes the tank wall heats to an average temperature of 266°F, shown as line AB, while there is essentially no heating of the H₂O₂ solution, shown as line AF. The line BC shows the continued rapid heating of that portion of the wall not wetted by the H₂O₂ solution resulting from the ullage. In 1.2 minutes the wall reaches an estimated 400°F, in 2.4 minutes 700°F, and 4.2 minutes 1200°F, the approximate melting point of aluminum. Thus we predict that the tank will fail in less than 5 minutes in such an intense, enveloping fire as is stipulated.

If, however, some mechanism not envisioned can cool the unwetted wall of the tank and it does not fail, then a continued sequence of events is as follows:

(a). $\theta = 0.72$ min.

When the wetted portion of the inside tank wall reaches a temperature corresponding to the normal boiling point of the H₂O₂ solution (258°F at $\theta = 0.72$ min.), either nucleate boiling (17) or a decomposition heat-transfer mechanism (15) begins. In either case, the capacity to transfer heat to the liquid greatly exceeds the incoming heat flux and the liquid is heated, as line FG shows.

(b). $\theta = 0.72$ to 13.2 min

As the H₂O₂ liquid heats along line FG, it expands (more rapidly than the tank) and the ullage decreases thus compressing the gas and increasing the pressure in the tank. We estimate that the tank pressure reaches 53.7 psia (relief pressure) when the average liquid temperature reaches 142°F. As the tank pressure increases, the saturation temperature of the H₂O₂ solution increases and the wetted-wall temperature adjusts upward to give the required heat flux from the wall to the liquid, line BE. Then

at $\theta = 13.2$ minutes, the wetted-wall temperature reaches 350°F and, as shown by the vertical dashed line in the Figure, the relief valve functions. However, vapor still remains in the tank at this time.

(c). $\theta = 13.2$ to 26.9 min

When the tank pressure reaches 53.7 psia, the average wetted-wall temperature remains at about 246°F as the H_2O_2 reaches 223°F , and the expanding liquid fills the tank, point G. H_2O_2 liquid vents, adding to the fire.

(d). $\theta = 26.9$ to 44.8 min

The H_2O_2 continues to heat until its saturation temperature at 53.7 psia is reached (point H). Explosive vapor then forms (explosive limit at 53.7 psia = 18.5 mole percent (16)) in a tank above its ignition temperature (302°F for inert materials such as aluminum (3)).

Insulated Tank - In a fire situation, insulated tanks have a decided advantage over bare tanks. This advantage derives from the opacity of the insulation to radiation; thus heat transmits through the insulation only by conduction. As shown in Figure 5, insulation reduces the heating rate of the tank wall. With the 2.76 -inch insulation, the average tank-wall temperature is estimated at 30 minutes as only 144°F assuming no heat loss to the liquid (line AC in Figure 5). For 1 inch insulation, it reaches an average of 266°F in 29.1 minutes to give an inside-wall temperature of 258°F , the normal boiling point of the H_2O_2 (see line AB). Alternately, if we assume that all of the heat transferred is dumped into the H_2O_2 solution, the temperature rise would be 2°F for the thick insulation and 4°F for the one inch insulation (line AD).

Such insulations as glass wool, 85% magnesia and rock wool exhibit thermal conductivity of about $.043 \frac{\text{Btu}}{(\text{hr}) \times (\text{ft}) (^{\circ}\text{F})}$, however the recommended maximum temperature for their use is only 500°F (18). In hydrocarbon fires, average environmental temperatures of

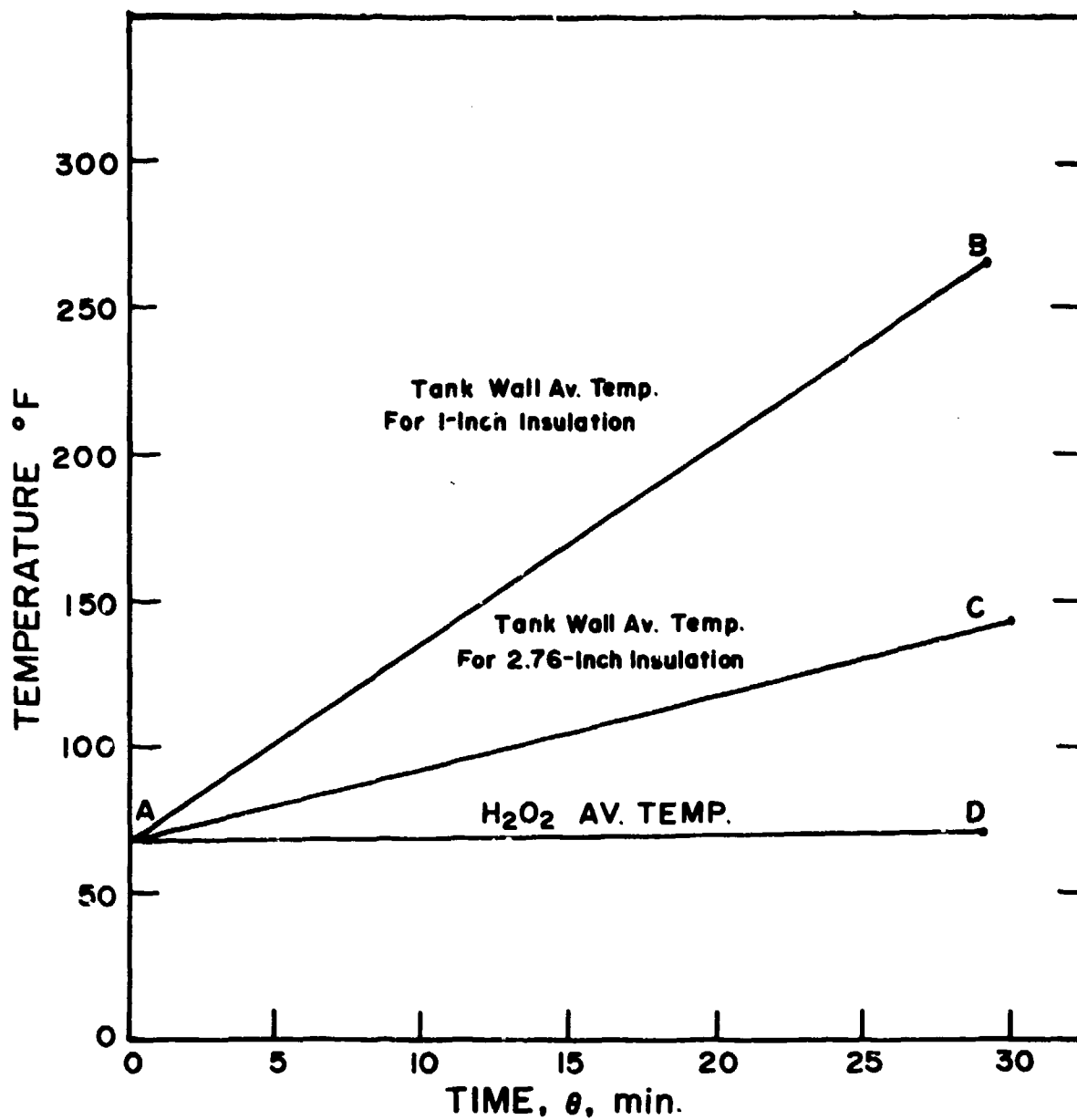


Fig. 5 - Temperature increase for insulated tanks

about 1700°F are estimated (12).

DISCUSSION

The data in Figure 3 show that 70 percent H_2O_2 solution free of impurities (Curve A) releases heat at a level which would allow ready dissipation even with insulation on the 4,000 gallon tank. For the convection only cooling mode (the conservative case) this Figure predicts that the H_2O_2 in a bare aluminum tank could reach a temperature of 257°F (125°C) before self heating occurs. The self-heating temperatures for the one-inch and 2.76-inch thick insulation cases are 222°F (106°C) and 197°F (92°C) respectively.

Should the H_2O_2 be contaminated so that the decomposition rate were five times (Curve B) that observed in our laboratory experiments, these self-heating temperatures would be somewhat lower. Thus, the critical temperature for the bare tank becomes 208°F (98°C), that for the tank with one inch of insulation becomes 170°F (77°C), and that for the tank with 2.76 inches of insulation becomes 142°F (61°C).

All of these temperatures are above ambient conditions found even in the tropics and hence should not rule out the use of insulation for containers of this size. This evaluation is valid if the peroxide is free from contaminants. The effect of higher decomposition rates on the self-heating temperature can be estimated by raising Curve A by the proper amount.

Insulated tanks demonstrate a distinct advantage over the bare tanks during exposure to an intense fire. The analysis illustrated in Figure 4 delineated several regimes of hazard for the bare tank. The first of these is early in the fire when we predict the unwetted wall of the tank would become very hot. Tests on 250 gallon steel LPG tanks by the Railroad Tank Car Safety Research and Test Project (12) found that the unwetted wall in an intense fuel fire reached 550°F (288°C) in two minutes and 800°F (427°C) in 4 minutes. Such temperatures, which support our analysis, would lead to rupture of the aluminum tank before the liquid phase absorbed sufficient

heat to expand and fill the ullage. Although the wetted wall can be kept at a modest temperature by nucleate boiling, no physical mechanisms can afford adequate cooling for the unwetted wall.

A second hazard regime occurs when the liquid fills the tank and liquid oxidizer is added to the fire. This will intensify the fire (raise the flame temperature). Since various H_2O_2 -organic mixtures detonate (3), such an event also cannot be ruled out at this stage.

The third hazard regime comes after some liquid has boiled off and been vented. Vapor again occupies a portion of the tank and vapor will vent. However, the concentration of the H_2O_2 in the vapor phase will exceed 18.8%, the lower limit for vapor phase explosion at the design relief pressure, 53.7 psia.

All of these hazardous regimes are avoided by adding insulation to reduce heat transfer from the fire to the tank and contents. Even though the wall temperature for the one inch insulated tank would reach the H_2O_2 boiling point in 30 minutes, termination of the fire at this time would preclude a significant rise in liquid temperature ($4^\circ F$ for 1 inch insulation). The margin between the liquid temperature and the self-heating temperature would be large for stabilized peroxide.

The advantage afforded by insulation during the fire situation considerably exceeds the disadvantage associated with insulation during normal storage. During a fire, the insulation comprises the major thermal resistance between the fire and the tank since radiation (about 90% of total) is the major mode of heat transfer. Thus, the low thermal conductivity of the insulation is controlling during a fire and the 2.76 inch insulation reduces the amount of heat transferred to about one percent that expected for the uninsulated tanks.

During normal storage, convection is the major heat transfer mode to dissipate heat from the tank. The exterior free convection film constitutes the major thermal resistance for transfer from the bare container and is a significant portion of the resistance for the

insulated tank. Thus, the insulation does not have the overriding control of heat transfer for normal storage that it does for the fire environment.

The decomposition of stabilized H_2O_2 , even at elevated temperatures, contributes much less heat than that derived from an external fire and this heat source has been disregarded in the heat transfer analysis.

Gas formation from peroxide decomposition will be slight. For example, the 4,000 gallon tank decomposing at the rate found in our studies would yield only 250 ft³/hr at the normal boiling point of 257°F (125°C). The vent requirement for the period "initial relief to shell full" is likewise low, 60 ft³/hr. The liquid vent requirement for the shell full regime would be 120 ft³/hr. If the tank should survive beyond the shell full stage and the heat from the fire was going into H_2O_2 vaporization, a vent capacity of $2.5-3.0 \times 10^5$ ft³/hr. would be necessary.

The concentration of the peroxide carried in a container can affect the degree of hazard. One aspect of the hazard is explosion of the vapor phase. Explosion requires a minimum hydrogen peroxide concentration in the vapor phase and thus depends on the temperature and concentration of the liquid phase generating the vapor. At one atmosphere pressure, 26 mole % and above will explode if initiated by a spark or a catalyst (3). Ninety wt-% H_2O_2 liquid forms a vapor with 26 mole % H_2O_2 at 243°F whereas 74 wt % H_2O_2 must be heated to its boiling point, 263°F, to attain this vapor concentration. Liquids with less than 74 wt. % H_2O_2 cannot reach the vapor explosion limit at one atmosphere pressure.

A change in system pressure alters the vapor explosion limit - increasing to 40 mole % H_2O_2 at a lower pressure of 0.1 atmosphere (3) and decreasing to 18.5 mole % H_2O_2 at 53.7 psia, the pressure of interest for this study (16). A 64 wt. % liquid H_2O_2 can attain a vapor concentration of 18.5 mole % H_2O_2 under equilibrium boiling conditions at this higher pressure. Thus peroxide at a lower concentration would have less hazard potential. A reduction in the tank relief pressure would add another

safeguard with respect to vapor explosions. By keeping below the critical vapor concentration, the hazard of a H_2O_2 vapor explosion toward the end of the fire would be eliminated.

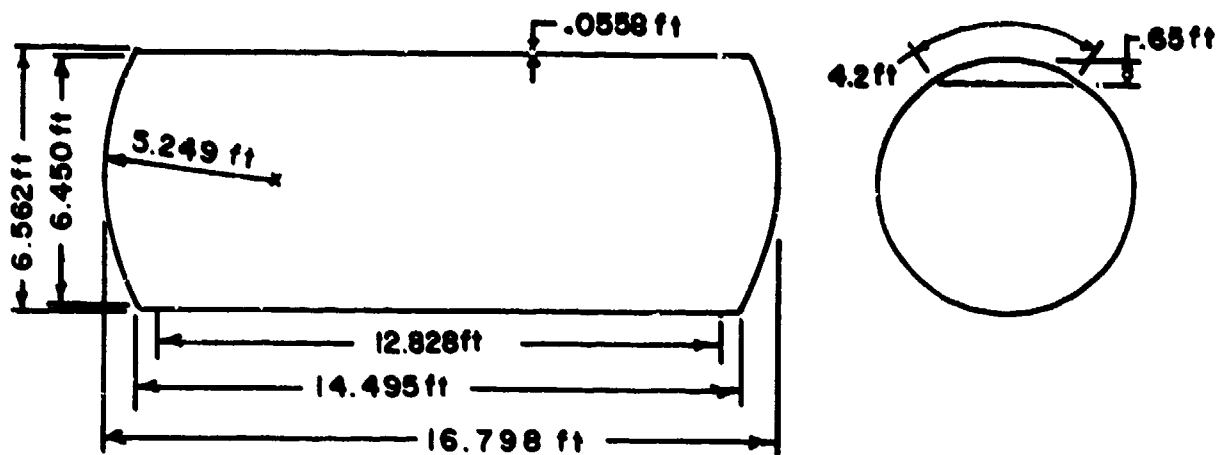
A lower peroxide concentration offers another safety advantage. The adiabatic decomposition temperature for 70 wt. % is 450°F. Peroxides with concentrations between 11.3 and 64.7 wt. % have a much lower adiabatic decomposition temperature, 212°F. The H_2O_2 heat of decomposition is not sufficient to evaporate all of the water in the product plus that formed from decomposition unless the concentration exceeds 64.7 wt. %. This factor would be particularly advantageous if the product spilled onto an active catalyst and rapid decomposition occurred.

Several minor factors affecting heat transfer have not been considered in these calculations. Examples of these factors are (1) the thermal resistance of the oxide film on the aluminum container, (2) the thermal resistance of air gap between the tank and the insulation, and (3) the short time required for the outside wall to reach steady-state conditions during a fire exposure.

RECOMMENDATIONS

1. Install insulation adequate to at least 1700°F on the 4,000 gallon aluminum shipping container. A one inch thickness with a thermal conductivity of 0.043 Btu/(hr)(ft)(°F) is appropriate. An equivalent combination of thickness and thermal conductivity could be substituted.
2. If full tank insulation is impractical, the unwetted portion of the tank should be covered with insulation.
3. Install a thermocouple to monitor the temperature of the tank contents.
4. Calculations be made to determine critical temperature rise rates to alert handlers to institute appropriate action.
5. Limit transport with aluminum containers to stabilized product with a concentration of 65% or less. This limitation would reduce the possibility of attaining the explosive vapor condition and would also limit the adiabatic decomposition temperature to 212°F (100°C) at one atmosphere pressure.
6. Reduce the pressure relief valve setting from 39 psig to 10 psig.
7. Examine the behavior of the tank cradle in an intense fire.

APPENDIX I
TANK DIMENSIONS



TANK VOLUME at 68°F = 490.4 cu ft = 3668 Gallons

INTERNAL SURFACE AREA at 68°F = 329.6 sq ft

EXTERNAL SURFACE AREA at 68°F = 335.3 sq ft

UNWETTED SURFACE AREA at 68°F = 60.4 sq ft

WETTED SURFACE AREA at 68°F = 269.2 sq ft

APPENDIX II - CALCULATIONS

Part I: SELF-HEATING OF TANK

In this section, we give the basis for the heating and cooling curves of Figure 3.

A. Heating Curves

For curve A, we use a decomposition rate of 0.9% per year at 77°F (25°C) as based on NRL measurements shown in Figure 2. If the heat of decomposition of 100% H₂O₂, H_D, is 1230 $\frac{\text{Btu}}{\text{lb}}$, an average of the values given by

Schumb, et al (3) and Shanley (4), the heat released by decomposition of 70 weight percent H₂O₂ aqueous solution, q_D, is

$$q_D = \frac{(0.70)(M)(P_t)(H_D)}{24 \times 100} \text{ Btu/hr}$$

where

M = weight of H₂O₂ solution in the tank filled at 68°F (20°C) with a 5% ullage, and is (490.4 cu.ft.) x (.95) x (80.4 $\frac{\text{lbs}}{\text{cu.ft.}}$) = 37,460 lbs.

P_t = peroxide decomposition rates in percent per day for various H₂O₂ temperatures as given in Fig. 2.

Values of q_D as a function of the average bulk H₂O₂ temperature for curve A are presented in Table 3.

Curve B in Fig. 2 is arbitrarily chosen as 5 times the decomposition rate of curve A.

B. Cooling Curves

1. Bare Tank (Curves 1 and 2 of Fig. 3) - For the bare tank, there are three resistances to the flow of heat from the liquid to the tank surroundings, which we can describe as R_A, R_B, and R_C. R_A is the thermal resistance to heat flowing between the liquid and the tank wall, R_B

TABLE 3

Heat Generated from 70 wt. % H_2O_2 with a Decomposition
Rate of 0.9% per Year at 25°C

<u>Temp.</u> <u>°C</u>	<u>Temp.</u> <u>°F</u>	<u>Decomp.</u> <u>Rate</u> <u>% per day</u>	<u>Decomp.</u> <u>Rate</u> <u>per hr.</u>	<u>Heat</u> <u>Released</u> <u>Btu/hr.</u>
25	77	.0024	1.0×10^{-6}	32.3
30	86	.0035	1.46×10^{-6}	47.1
35	95	.0050	2.08×10^{-6}	67.1
40	104	.0073	3.04×10^{-6}	98.0
45	113	.0104	4.33×10^{-6}	140
50	122	.0150	6.25×10^{-6}	202
55	131	.0217	9.04×10^{-6}	292
60	140	.0313	13.0×10^{-6}	419
70	158	.0650	27.1×10^{-6}	874
80	176	.135	56.3×10^{-6}	1820

is the resistance through the tank wall, and R_C is the resistance between the tank and its surroundings. When we evaluate these resistances, we find that R_C is enough larger than R_A and R_B that the latter two can be ignored in determination of the cooling curves. We proceed to justify this assumption.

The resistance to heat flowing from the liquid H_2O_2 to the tank wall, R_A , is the most difficult to estimate. According to Ostrach (19), study of heat transfer by natural convection in enclosures has attracted far less attention than that from the outside of vessels to their surrounding fluids. He attributes this fact to the added complication that in enclosures the boundary layer encloses a core region and the two are closely coupled. In lieu of correlations for horizontal cylinders we resort to the closest available model which has received analytical study. We estimate R_A for the cylindrical tank by using the data for a square cross section, according to Newell and Schmidt (20) as Ostrach describes. We do this by equating the tank diameter to one side of the square. In the Newell-Schmidt correlation, the Nusselt number, Nu_d , is expressed as a function of the Grashof number, Gr_d , as follows:

$$\overline{Nu}_d = 0.0547 (Gr_d)^{0.397}$$

where*

$$\overline{Nu}_d = \overline{h}_d D_i / k_f$$

*NOTE: Physical properties of H_2O_2 are taken from references (3), (21) and (22). When property extensions are necessary, methods are applied as recommended by Reid and Sherwood (23) or by Hougen and Watson (24).

and

$$Gr_d = \frac{D_i^3 \rho_f^2 g \beta_f \Delta t_{b-i}}{\mu_f^2}$$

Hence, $\bar{h}_D = 83.9 \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(^\circ\text{F})}$. Since the film resistance is the reciprocal of its conductance, the film resistance times the outside area becomes

$$\begin{aligned} A_O R_A &= \frac{A_O}{(\bar{h}_D)(A_i)} \approx \frac{D_O}{(\bar{h}_D)(D_i)} \\ &= \frac{6.562}{(83.9 \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(^\circ\text{F})}) 6.45 \text{ ft}} \\ &= 0.012 \frac{(\text{hr})(\text{ft}^2)(^\circ\text{F})}{\text{Btu}} \end{aligned}$$

The resistance to the flow of heat through the tank wall, R_B , depends on properties and condition of the aluminum wall. If we do not account for any oxide film, then R_B times outside area is

$$A_O R_B = \frac{x_w D_O}{k_{av} D_{av}} = 4.8 \times 10^{-4} \frac{(\text{hr})(\text{ft}^2)(^\circ\text{F})}{\text{Btu}}$$

for

$$t_{av} = 1/2 (88 + 78) = 83^\circ\text{F}$$

To estimate R_C , the thermal resistance to heat flow from the tank wall to the surroundings, we consider heat energy transferral both by free convection and by radiation. These two mechanisms operate in parallel, so that

$$A_O R_C = \frac{A_O}{(\bar{h}_c + \bar{h}_r) A_O}$$

According to Kreith (17), if the Rayleigh number ranges from 10^9 to 10^{12} - for our case, the range is 10^9 to 10^{10} - we may estimate \bar{h}_c for air by

$$\bar{h}_c = 0.18 \Delta t_{o-a}^{1/3}$$

Values of \bar{h}_c so obtained are given in Table 4.

The coefficient for radiation, \bar{h}_r is determined in two steps. First, heat energy lost by radiation from the tank is estimated by the equation (25),

$$q_{rad} = \epsilon_1 \sigma (T_o^4 - T_a^4) A_{ww}$$

Then, with values for the radiation energy interchange, values of \bar{h}_r are determined by

$$\bar{h}_r = \frac{q_{rad}}{A_{ww}(t_o - t_a)}$$

Values of \bar{h}_r are given in Table 4 as are those for \bar{h} , the sum of $\bar{h}_c + \bar{h}_r$, from which values of $A R_c$ are calculated to range from 1.7 to 0.7 (hr)(ft²)(°F)/Btu.

Thus, R_c is greater than R_a by two orders of magnitude and greater than R_B by three, and heat lost from the bare tank is

$$q_1 = \bar{h} A_{ww} \Delta t_{o-a}$$

Values of q_1 for various assumed outside wall temperatures are presented in Table 4 and are plotted as curve 1 in Figure 3. Notice that since we have assumed no resistance to heat flow from the liquid film or across the tank wall, R_A or R_B , the H_2O_2 average temperature and the outside wall temperature become the same, and this applies in Figure 3. For heat lost by radiation, we assume the tank as a gray body radiating to its surroundings as a black body at 78°F, such conditions as exist on deck or in a large enclosure.

TABLE 4 - Heat Lost from Bare Tank

t_o (°F)	Δt_{o-a} (°F)	\bar{h}_c	$\frac{qL^2}{A_o}$	\bar{h}_r	\bar{h}	A_{oC}	A_{oC}^*	q_l	q_l^*
87	9	.37	1.97	.22	.59	1.69	2.70	1450	913
96	18	.47	4.03	.22	.69	1.45	2.13	3400	2320
105	27	.54	6.20	.23	.77	1.30	1.85	5700	4000
114	36	.59	8.47	.24	.83	1.20	1.69	8190	5840
123	45	.64	10.9	.24	.88	1.14	1.56	10900	7900
132	54	.68	13.4	.25	.93	1.08	1.47	13800	10100
141	63	.72	16.0	.25	.97	1.03	1.39	16700	12400
150	72	.75	18.7	.26	1.01	.99	1.33	19900	14800
159	81	.78	21.6	.27	1.05	.95	1.28	23300	17300
168	90	.81	24.5	.27	1.08	.93	1.23	26600	20000
177	99	.83	27.3	.28	1.11	.90	1.20	30100	22600
186	108	.86	30.9	.29	1.15	.87	1.16	34000	25500
220	142	.94	44.5	.31	1.25	.80	1.06	48600	36700
240	162	.98	53.5	.33	1.31	.76	1.02	58100	43500
260	182	1.02	63.3	.35	1.37	.73	.98	68300	50900
280	202	1.06	73.9	.37	1.43	.70	.94	79100	58700
300	222	1.09	85.4	.38	1.47	.68	.92	89400	66300

However, for curve 2, we assume that no heat is lost by radiation and that it is lost only by free convection, q^*_1 , as shown in Table 4.

When a thermal insulation is added to the outside of the tank, it has a resistance, R_I , of the same order of magnitude as exists from its outer surface to the air, k_c . However, as for the bare tank, R_A and R_B may be ignored. Then the total resistance to heat flow from the H_2O_2 is

$$R_T = \frac{1}{(\bar{h}_c + \bar{h}_r) A_I} + \frac{x_I}{k_I A_a}$$

The total heat lost from the insulated tanks, q_1 , based on the outside area A_I of the insulation is

$$q_1 = \frac{\Delta t_{s-a}}{R_T}$$

Values are given in Table 5 for the 1-inch insulation both with and without radiation losses included, where $A_I = 281 \text{ ft}^2$. The Table also gives the same information for the 2.76-inch insulation.

Part II: FIRE INVOLVEMENT

As is evident in Figures 4 and 5, the presence of insulation on the tank affords protection in fire situations. Insulated tanks with either 2.76 or 1.0 inches of suitable insulation are protected for 30 minutes and more in an intense fire, yet failure of a bare tank is predicted in less than 5 minutes. In the estimations that follow, we assume the heat flux in the fire is 34,500 Btu/(hr)(ft²) to the bare tank regardless of direction.

A. Bare Tank

1. Tank walls heat with negligible heat of H_2O_2 - In the first heating phase, designated as line AB in Figure 1, the tank walls rise in temperature from 68 to an average of 266°F. The temperature drop across the

TABLE 5 - Heat Lost from Insulated Tank

t_b (°F)	Δt_{O-a} (°F)	Δt_{I-a}	\bar{h}_C	$\frac{Q_{rad}}{A}$	\bar{h}_I	AR_T (Rad.)	AR_T (No Rad.)	q_l (Rad.)	q_l (No Rad.)
1-inch Insulation*									
87	9	4	.29	3.66	.92	2.79	5.41	906	467
105	27	11	.40	10.3	.93	2.71	4.46	2800	1700
123	45	20	.49	19.1	.96	2.65	4.00	4800	3160
141	63	28	.55	27.4	.98	2.61	3.78	6800	4680
159	81	36	.59	36.0	1.00	2.59	3.65	8800	6240
177	99	44	.64	45.0	1.02	2.56	3.52	10900	7900
220	142	62	.71	66.6	1.07	2.52	3.37	15800	11800
240	162	71	.75	78.2	1.10	2.50	3.29	18000	13800
260	182	80	.78	90.2	1.13	2.48	3.24		15800
2.76-inch Insulation**									
87	9	1	-	.91	.91	6.63	-	398	-
105	27	3	.26	2.74	.91	6.38	9.37	1240	844
123	45	4.5	.30	4.12	.92	6.35	8.86	2080	1490
141	63	6	.33	5.52	.92	6.33	8.56	2920	2160
159	81	8	.36	7.40	.93	6.31	8.31	3760	2860
177	99	10	.39	9.30	.93	6.31	8.09	4600	3590
220	142	14	.43	13.2	.94	6.26	7.86	6650	5290
240	162	16	.45	15.1	.95	6.24	7.75	7610	6120
260	182	18	.47	17.1	.95	6.23	7.66	8560	6960

$$* AR_I = 1.96 \frac{(hr)(ft^2)(°F)}{Btu}$$

$$** AR_I = 5.53 \frac{(hr)(ft^2)(°F)}{Btu}$$

tank wall is

$$\Delta t_{i-o} = \frac{(34,500 \frac{\text{Btu}}{(\text{hr})(\text{ft})^2}) (0.0558 \text{ ft})}{(118.5 \frac{\text{Btu}}{(\text{hr})(\text{ft})(^\circ\text{F})}) (1 \text{ ft}^2)} = 16^\circ\text{F}$$

and at point B the inside wall temperature is 258°F , the saturation temperature of 70 wt % H_2O_2 at 1 atmosphere (14.7 psia) pressure.

During this period of some 0.72 minute, essentially all of the heat transferred from the fire heats the tank wall. This is because the resistance to the flow of heat from the tank wall to the liquid exceeds that of the flow from the fire to the bare wall by about an order of magnitude. The average wall resistance, R_B , as based on the outside area of the tank is

$$\begin{aligned} A_{O B} R_B &= \frac{x_w A_O}{k_w A_{av}} \approx \frac{x_w D_O}{k_w D_{av}} = \frac{(0.0558 \text{ ft}) (6.562)}{(118.5 \frac{\text{Btu}}{(\text{hr})(\text{ft})(^\circ\text{F})}) (6.506)} \\ &= 4.7 \times 10^{-4} \frac{(\text{hr})(\text{ft}^2)(^\circ\text{F})}{\text{Btu}} \end{aligned}$$

for a $t_w = 1/2(266 + 68) = 167^\circ\text{F}$.

When we assume free convection of an enclosure according to Ostrach (19) as before for a square cross section and use a maximum temperature difference between the wall and fluid to give a minimum thermal resistance for the liquid, the heat conductance from the wall to the liquid, h_D is

$$\bar{h}_D = \left(\frac{k_f}{D_i} \right) (0.054) \left(\frac{D_i^3 \rho^2 g \beta_f \Delta t_{i-b}}{\mu_f^2} \right)^{0.397}$$

Using $\Delta t_{i-b} = 258 - 68 = 190^\circ\text{F}$, \bar{h}_D becomes $267 \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(^\circ\text{F})}$

and the thermal resistance from the wall to the H_2O_2 is

$$A_o R_A = \frac{A_o}{h_D A_i} = \frac{6.562}{(267)(6.450)} = 0.0038 \frac{(\text{hr})(\text{ft}^2)(^\circ\text{F})}{\text{Btu}}$$

$$\text{Thus, } \frac{R_A}{R_B} = \frac{0.0038}{4.7 \times 10^{-4}} = 8, \text{ about 1 order of magnitude.}$$

Then, accordingly, the heat required to raise one square foot of aluminum wall from 68° to 266°F with no heat loss is

$$Q = C_{p_{av}} \Delta t_{inc} W_{av}$$

For a $t_{av} = 1/2(266 + 68) = 167^\circ\text{F}$, we find

$$Q = (9.419)(0.2212)(198) = 412.5 \text{ Btu.}$$

Since the incoming heat energy is $34,500 \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)}$, the time for it to pass to the wall is

$$\theta = \frac{Q}{q/A} = \frac{412.5 \text{ Btu}}{34,500 \frac{\text{Btu}}{\text{hr}}} = 0.012 \text{ hrs} = 0.72 \text{ min}$$

2. Failure of tank wall in ullage space - Since there is an ullage of 5% when the tank is filled, assumed at 68°F (20°C) and 1 atm. pressure, about 60.4 ft^2 of the tank wall is not wetted. As a result, the incoming heat energy from the fire to this section of wall is transferred away at only a fraction of its incoming rate. For example, the maximum heat transferred down the wall from the unwetted to the wetted section is at a maximum temperature difference. If we assume this difference as $400 - 266 = 134^\circ\text{F}$ for a length of 6 inches, the heat transferred down the wall, q_k becomes

$$q_k = \frac{k_w A \Delta t}{\Delta X} = \frac{(125 \frac{\text{Btu}}{\text{hr ft } ^\circ\text{F}}) (.0558 \text{ ft}) (1 \text{ ft}) (134^\circ\text{F})}{(0.5 \text{ ft})}$$

$$= 1900 \frac{\text{Btu}}{\text{hr}}$$

for a width of 1 ft. This loss amounts to about 5% of the incoming energy. Further, if we assume black-body conditions, the maximum energy radiated from the unwetted surface is

$$\frac{q_{\text{rad}}}{A} = \sigma (T_{\text{uw}}^4 - T_{\text{H}_2\text{O}_2}^4) F = 0.171 [(8.6)^4 - (5.28)^4]$$

$$= 800 \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)}$$

This is about 2.3% of the total incoming energy. Thus, we estimate that heat lost from the unwetted portion of the tank wall loses less than 10% of that added by the fire. So the unwetted wall rapidly increases in temperature. Thus, by disregarding losses, we determine the time needed to heat the unwetted tank wall from 68°F to 400°, 700°, and 1200°F:

$$\theta = \frac{\text{heat capacity of tank wall}}{\text{rate of incoming heat energy}} = \frac{Q}{q}$$

For one square foot of wall surface, the weight at 68°F is

$$W_{68} = (\text{area}) (\text{thickness}) (\text{density})$$

$$= (1 \text{ ft}^2) (.0558 \text{ ft}) (168.8 \frac{\text{lb}}{\text{ft}^3})$$

$$= 9.419 \text{ lbs.}$$

As the tank wall temperature increases, it expands. This expansion is

$$L_t = L_{68} [1 + \alpha (t-68)(10^{-6})]$$

at 400 and 700°F respectively,

$$L_{400} = L_{68} (1.0045) \text{ and}$$

$$L_{700} = L_{68} (1.0066).$$

Further

$$W_{400} = \frac{W_{68}}{(L_{400})^3} = \frac{9.419 \text{ lbs}}{(1.0045)^3} = 9.293 \text{ lbs and}$$

$$W_{700} = \frac{W_{68}}{(L_{700})^3} = \frac{9.419 \text{ lbs}}{(1.0092)^3} = 9.164 \text{ lbs.}$$

The heat energy to increase the wall temperature from 68 to $t^\circ\text{F}$ is $(W_{av}) (C_{pav}) (\Delta t_{inc})$, and accordingly, for the range 68 to 400°F: $Q = 1/2(9.419 + 9.293) (.2266) (332) = 702 \text{ Btu}$, and for 68 to 700°F: $Q = 1/2(9.419 + 9.164) \times (.2365) \times (632) = 1389 \text{ Btu}$. Hence, the times required to heat the unwetted wall to specific temperatures are estimated as

$$\theta_{400} = \frac{(702 \text{ Btu}) (60 \frac{\text{min}}{\text{hr}})}{(34,500 \frac{\text{Btu}}{\text{hr}})} = 1.22 \text{ min,}$$

$$\theta_{700} = \frac{(1389) (60)}{34,500} = 2.42 \text{ min, and}$$

$$\theta_{1200} \cong 2.42 \frac{1200-68}{700-68} = 4.3 \text{ min.}$$

In Figure 3, the lines BC, CD, and DK show these times and temperatures. The yield strength of 99.6 aluminum (28) decreases as its temperature increases:

Temp., °F	75	300	400	500	600	700
Yield strength, psi	5000	3500	3000	2000	1500	1000
Percent of 75°F	100%	70%	60%	40%	30%	20%

and the metal melts at c.a. 1195°F. Thus, we predict a failure by melting for the intense fire situation examined here.

3. Heating of the H₂O₂ solution - If "bumping" of the liquid, a smaller fire than assumed, or some other unenvisioned mechanism results in a nonfailure of the bare tank as we predict, then the 70 wt % H₂O₂ in the tank begins to heat as the wetted section of wall reaches about 258°F, the normal boiling point of the H₂O₂ solution (3). According to Rohsenow (29), nucleate boiling would begin at this approximate wall temperature. In addition, Sanborn, et al, (15) describe a decomposition heat-transfer mechanism which begins at a somewhat lower temperature for a 90% H₂O₂ aqueous solution. Either of these mechanisms would easily accommodate the incoming heat energy flux.

Consider the ullage of the tank. For 68°F, Appendix I shows the ullage as 24.47 cu. ft. In a fire, this ullage first increases as the walls heat and the liquid does not. At point B of Fig. 4, the ullage becomes

$$(24.47 \text{ ft}^3) [1 + (13.3) (198) (10^{-6})]^3 = 24.66 \text{ ft}^3.$$

After point B, the liquid expands more rapidly than the wall, and the ullage decreases. Our interest is to determine if the ullage change creates a tank pressure of 53.7 psia, the pressure which actuates the relief valve system. To do this, we first estimate the volume change at Point B needed to produce the actuating pressure by the perfect gas law

$$V_{68} = 24.75 \text{ ft}^3 \left(\frac{14.7}{53.7} \right) = 6.78 \text{ ft}^3.$$

Now we correct this volume for increasing temperature again assuming the ideal gas law.

Vapor Temp., °F	68	176	237	338
Ullage, ft ³	6.775	8.161	8.944	10.24

and choose the vapor temperature as 237°F by the estimate that

$$t_{\text{vapor}} = 1/2 \left[\frac{2}{3} (230-68)_{\text{liquid}} + 1/2 (258 + 238)_{\text{wall}} \right] \\ = 237^{\circ}\text{F}.$$

This prediction gives a 9.0 cu. ft. ullage, along with a vapor temperature of 237°F and an average wall temperature of 346°F. For these conditions the original 37,460 lbs of H₂O₂ has expanded to 479.9 cu. ft., a density of $78.05 \frac{\text{lb}}{\text{ft}^3}$,

corresponding to a temperature of 142°F. Thus, when the H₂O₂ solution average temperature reaches 142°F, the relief-system functions. The time required for a Δt of 74°F is

$$\theta = \frac{M C_{pH} \Delta t}{A_{ww} (q/A)} = 12.7 \text{ min.}$$

Thus, the valve functions at about $12.7 + .72 = 13.4 \text{ min.}$

The estimated time for the liquid to fill the tank is

$$\frac{Q}{q} = \frac{W C_{pH} \Delta t}{(q/A) (A_{wa})} (60) = 17.9 \text{ min}$$

where: Q = heat energy to heat H₂O₂ to 223°F

$$A_{wa} = \text{av. wetted area} - 1/2(284.6 + 330.9), \text{ ft}^2$$

$$\Delta t = 223 - 142 = 81^{\circ}\text{F}.$$

We obtain the temperature, 223°F, at which the tank goes liquid full by considering the density of the 70 wt % H₂O₂ solution. When the tank is filled its volume is

$$V_{68} [1 + \alpha (346-68)]^3 = 496 \text{ ft}^3$$

where, V_{68} = tank volume at 68°F, 490.4 cu ft.

The density of the H_2O_2 then is

$$\rho_f = \frac{M}{V_{346}} = \frac{37,460 \text{ lbs}}{496 \text{ ft}^3} = 75.5 \frac{\text{lb}}{\text{ft}^3}$$

and 70 wt % H_2O_2 has this density at 223°F.

The time to heat the liquid from 142° to 223°F is

$$\frac{Q}{q} = \frac{(37,460 \text{ lbs}) (0.768 \frac{\text{Btu}}{\text{lb}^\circ\text{F}}) (223-142) (60 \frac{\text{hr}}{\text{min}})}{(34,500 \frac{\text{Btu}}{\text{hr ft}^2}) (307.8 \text{ ft}^2)}$$

$$= 13.7 \text{ min.}$$

Therefore, the total time is $13.2 + 13.7 = 26.9 \text{ min.}$

The liquid would reach its boiling point at 53.7 psia, if we disregard the overflow, in an additional 18 minutes producing explosive vapors.

$$\frac{(37,460 \text{ lbs}) (0.791 \frac{\text{Btu}}{\text{lb}^\circ\text{F}}) (338^\circ-223^\circ\text{F}) (60)}{(34,500 \frac{\text{Btu}}{\text{hr ft}^2}) (330.9 \text{ ft}^2)} = 17.9 \text{ min.}$$

B. Insulated tank

Since insulation, we assume, is opaque to radiant energy, a heat flux of 34,500 Btu/(hr)(ft²) does not apply. To determine a heat flux, we consider the exposed insulation temperature as 1700°F, the estimated temperature of the fire environment (12). We assume further that the thermal resistance of the insulation is controlling. Then the heat flux to the tank is

$$\frac{q}{A_o} = \frac{\Delta t_I}{\frac{X_I A_o}{k_I A_a}}$$

For 1-inch insulation, the flux is $850 \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)}$; while for 2.76-inch, it is $320 \text{ Btu}/(\text{hr})(\text{ft}^2)$.

With these fluxes, first assume the extreme that all of the incoming energy goes to heat the tank wall, and calculate the time to heat the wall from 78 to 266°F, the approximate condition for nucleate boiling or decomposition heat transfer mechanisms. These times are estimated by

$$\theta = \frac{W_{\text{av}} C_{pA1} (266-78^\circ\text{F})}{q/A_o}$$

and are 28.2 minutes and 75 minutes for the 1.0- and the 2.76-inch insulation, respectively. For the thicker insulation, the wall temperature at 30 minutes is 153°F. These values are shown in Fig. 5 as points B and C, where B is for the 1-inch insulation.

Now consider the temperature rise of the H_2O_2 solution. In this case, assume that all the heat energy goes to the liquid. For the 37,460 pounds of H_2O_2 with an average specific heat of $0.745 \text{ Btu}/(\text{lb})(^\circ\text{F})$ and an area of 274 ft^2 , a H_2O_2 temperature increase of 4°F for the 1-inch and 2°F for the 2.76-inch insulation is estimated.

With these temperatures for the wall and the liquid, the thermal resistance of free convection in the enclosure is estimated as before to give values much less than those for the insulation. Thus, the original assumption that the insulation controls the heat transfer from the fire to the tank and contents is satisfactory even for the extremes assumed.

Part III: LIST OF SYMBOLS

A - area, ft^2

A_a - average area of insulation normal to heat flow

- A_{av} - average area of tank wall, $[1/2(A_i + A_o)]$
 A_I - outside area of tank insulation
 A_i - area, tank inside
 A_o - area, tank outside
 A_{ww} - outside area of tank less the area unwetted by the H_2O_2 solution; $335-61 = 274 \text{ ft}^2$ at 68°F
 C_{pAl} - average heat capacity of aluminum over a temperature range $\frac{\text{Btu}}{(\text{lb})(^\circ\text{F})}$
 C_{pH} - average heat capacity of 70% H_2O_2 over a temperature range $\frac{\text{Btu}}{(\text{lb})(^\circ\text{F})}$
 D_{av} - average diameter of tank, ft $[1/2(D_i + D_o)]$
 D_i - inside diameter of tank, ft
 D_o - outside diameter of tank, ft
 F - view factor = 1, dimensionless
 Gr_d - Grashof number
 H_D - H_2O_2 heat of decomposition, Btu/lb
 L_t - length at specified temperature, ft
 M - weight of H_2O_2 in tank, lb
 \overline{Nu}_d - Nusselt number
 P_t - rate of H_2O_2 decomposition at specified bulk liquid temperature, %/day
 Q - quantity of heat, Btu
 R - thermal resistance to heat flow, $\frac{(\text{hr})(^\circ\text{F})}{\text{Btu}}$

- R_A - thermal resistance between liquid and tank wall
- R_B - thermal resistance through tank wall
- R_C - thermal resistance between tank and surroundings
- R_I - thermal resistance through insulation
- R_T - thermal resistance, total
- T - absolute temperature, °R
- T_a - air temperature, absolute = $460 + 78 = 538^\circ\text{R}$
- $T_{\text{H}_2\text{O}_2}$ - H_2O_2 surface temperature, absolute
- T_o - outside wall temperature, absolute
- T_{uw} - inside temperature of unwetted tank wall, absolute
- W_t - weight of 1 ft^2 of aluminum wall at specified temperature; 9.419 lb 68°F
- W_{av} - average weight of 1 ft^2 of aluminum wall over a temperature range
- V - volume, ft^3
- g - acceleration of gravity, $32.2 \frac{\text{ft}}{\text{sec}^2}$
- h - heat transfer coefficient $\frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(^\circ\text{F})}$
- \bar{h} - sum of $\bar{h}_c + \bar{h}_r$
- \bar{h}_c - average heat transfer coefficient for free convection
- \bar{h}_D - liquid film coefficient of heat transfer
- \bar{h}_r - heat transfer coefficient for radiation
- k_{av} - thermal conductivity of aluminum at t_{av} ;
 $118.5 \frac{\text{Btu}}{(\text{hr})(\text{ft})(^\circ\text{F})}$

- k_f - thermal conductivity of H_2O_2 at t_f ;
 $0.346 \frac{\text{Btu}}{(\text{hr})(\text{ft})(^\circ\text{F})}$
- k_I - insulation thermal conductivity; used value of
 $0.043 \frac{\text{Btu}}{(\text{hr})(\text{ft})(^\circ\text{F})}$
- k_w - thermal conductivity of aluminum at t_w
- q/A - heat flux; 34,500 $\frac{\text{Btu}}{(\text{hr})(\text{ft})^2}$ for bare tank exposure to fire
- q - heat transfer rate, Btu/hr
- q_D - rate of heat release by H_2O_2 decomposition, Btu/hr
- q_k - heat transfer rate along tank wall
- q_l - heat lost from tank, Btu/hr
- q_l^* - heat lost from tank by free convection
- q_{rad} - net radiation interchange of the tank with surroundings, Btu/hr
- t - temperature, $^\circ\text{F}$
- t_a - temperature of air
- t_{av} - average temperature of aluminum
- t_b - temperature of bulk H_2O_2
- t_F - temperature of liquid H_2O_2 film at tank wall,
 $\frac{t_i + t_b}{2}$
- t_i - temperature of tank inside wall
- t_o - temperature of tank outside wall
- t_w - average tank wall temperature

- Δt - temperature difference or change, °F
 Δt_{b-i} - temperature difference, bulk liquid to inside wall
 Δt_{I-a} - temperature difference, outside of insulation to air
 Δt_I - temperature difference across insulation; used 1700-68 = 1632°F for fire exposure
 Δt_{inc} - temperature increase of tank wall
 Δt_{i-b} - temperature difference, inside wall to bulk H₂O₂
 Δt_{i-o} - temperature difference across tank wall
 Δt_{o-a} - temperature difference between outside tank wall and air, 78°F assumed for t_a
 X_I - insulation thickness, ft
 X_w - tank wall thickness, 0.0558 ft

Greek Symbols

- α - coefficient of linear expansion for 99.6% Al (27), $13.6 \times 10^{-6} \text{ } ^\circ\text{F}^{-1}$
 β_f - coefficient of thermal expansion of fluid; values for water used (17), $1.6 \times 10^{-4} \text{ } ^\circ\text{F}^{-1}$
 ϵ_1 - emissivity, dimensionless; 0.2 used for heavily oxidized aluminum surface (26); 0.85 used for insulation
 θ - time period, minutes
 σ - Stefan-Boltzman constant; $0.1714 \times 10^{-8} \frac{\text{Btu}}{(\text{hr})(\text{ft}^2)(^\circ\text{R})^4}$
 ρ_f - H₂O₂ density
 μ_f - viscosity of H₂O₂ at t_f ; $7.25 \times 10^{-4} \frac{\text{lb}}{(\text{ft})(\text{sec})}$ at 83°F

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